

SELECTIVE PRODUCTION OF ALPHA OLEFINS FROM SYNTHESIS
GAS OVER ZnO SUPPORTED Pd-Fe BIMETALLICS

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INTRODUCTION

Olefins are basic raw materials for a wide variety of commercial processes within the chemical industry. A synthesis-gas-based route to low molecular weight α -olefins would provide the chemical industry with an alternative route to raw materials in the advent of future petroleum shortages or price increases.

The catalytic production of α -olefins from synthesis gas has been the subject of many investigations over the past 50 years.(1,2) It has been established that, in some systems, olefin selectivity can be enhanced through the addition of various promoters such as K, Mn, Ti, or Zn.(1,3-7) Olefin selectivity can also be dependent on process parameters such as temperature, pressure, conversion levels, or feed compositions.

Recent reports in the literature indicate that supported Fe-containing bimetallics may also be selective for the production of olefins from synthesis gas.(8) This study reports the use of Pd-Fe bimetallics supported on ZnO for the selective production of olefins from synthesis gas.

EXPERIMENTAL

Catalyst Preparation

The majority of catalysts used in this study were prepared by using aqueous co-impregnation with excess solvent. The nitrate salts of the desired metals ($\text{Pd}(\text{NO}_3)_2$, Alpha Products or $\text{Fe}(\text{NO}_3)_3$, Mallinckrodt) were dissolved in excess H_2O at room temperature. It was noted that if acetate salts were used for the metal source or if acetate impurities were present on the support material, the samples which resulted were totally inactive under the conditions employed in this study. For Mössbauer studies, isotopically enriched ^{57}Fe was obtained from Oak Ridge National Laboratory as Fe_2O_3 . This material was added to a HNO_3 solution, the solution was evaporated to near dryness twice, and then the residue was dissolved in H_2O . A sufficient amount of this solution was added to the impregnation solution to achieve approximately 50% enrichment in ^{57}Fe .

The solution containing the metals for impregnation was added to the ZnO support (Alpha Products, BET S.A. $7 \text{ m}^2\text{g}^{-1}$) at ambient temperature, and then the excess H_2O was removed by gentle heating in air. The samples were frequently stirred to ensure uniform impregnation. Following impregnation, the samples were calcined at 200-300°C for 3 hours to decompose residual nitrates. Metal loading levels were determined by using atomic absorption spectroscopy.

XPS measurements were made by using a PHI Model 550 ESCA/SAM spectrometer with a base pressure of 2×10^{-10} torr. All data were obtained at room temperature by utilizing unmonochromatized Mg K α radiation ($h\nu = 1253.6 \text{ eV}$) and an analyzer resolution of 0.3 eV. The Zn $2p_{3/2}$ peak was used as an internal standard for the determination of binding energies. In previous studies, this peak was found to have a binding energy of 1021.8 eV.(9)

Mössbauer spectra were obtained by using a Ranger Scientific MS-900 spectrometer equipped with a ^{57}Co -Rh source. All isomer shifts were measured relative to this source. The spectrometer was operated in the constant acceleration-flyback

mode so that only a single spectrum was recorded per scan. The velocity scale was calibrated by using an NBS-calibrated Fe foil absorber.

Catalyst Evaluation

All catalyst evaluations were conducted in a high-pressure-plug-flow reactor system. For a typical run, 1 mL of sample (14X40 standard mesh) was loaded into a reactor tube that was constructed from standard 1/4" stainless steel, high-pressure tubing. Prior to catalytic evaluation, the samples were reduced at 100 psig and at 300°C for 1 hour in a flow of H₂ or H₂/CO (Matheson Gas Ultra High Purity H₂, Matheson Purity CO). The feed gas was passed through an activated carbon bed at 130°C to remove metal-carbonyl impurities. Feed compositions were controlled by using Brooks mass flow controllers capable of operation up to 1500 psig. Reaction products were analyzed by using an on-line gas chromatograph fitted with a Chromosorb 102 (TM) column. Periodically, samples were analyzed off-line by GC-MS to verify product assignments. To ensure accurate rate measurements, space velocities were adjusted to keep CO conversion levels below 5%.

RESULTS AND DISCUSSION

Following an initial prereduction, the Fe/ZnO and Pd, Fe/ZnO samples were active catalysts at 300°C and at 100 psig for the conversion of synthesis gas to hydrocarbons in the C₁-C₅ range. The olefin fraction was typically in excess of 50 wt% of the observed products for the unpromoted catalysts. In the C₂-C₅ range, propene was the major component, with typical propene/propane ratios of 8-10. The influence of pretreatment conditions, metal loading levels, temperature, and H₂/CO ratio on catalytic activity and selectivity to olefins was investigated. The results of these studies are summarized below.

Catalyst Pretreatment

The catalytic activity of a 1% Pd, 0.3% Fe/ZnO sample was dependent on the nature of the pretreatment procedure. Samples reduced in a 1:1 H₂/CO feed at 100 psig and at 220°C for 1 hour were inactive for the conversion of synthesis gas. However, reduction in H₂/CO at 100 psig and at 260°C for 1 hour was sufficient for catalyst activation. Furthermore, after reduction at 260°C, the catalysts were active for the conversion of synthesis gas at 220°C.

Reduction at 220°C and at 100 psig in H₂ was comparable to reduction in H₂/CO at 260°C. Pretreatment above 300°C resulted in irreversible catalyst deactivation.

XPS spectra were obtained following reduction at various pretreatment temperatures. The results of this study are summarized in Table 1. Following reduction, the Pd 3d_{5/2} peak shifted to 336.0 eV, a value approximately 1 eV higher in binding energy than that of Pd metal.⁽¹⁰⁾ This shift in Pd binding energy has been observed in the absence of Fe and can be attributed to a strong interaction between Pd and reduced ZnO.⁽¹⁰⁾ As in a previous study on Pd/ZnO (ref. 10), a shoulder was observed on the Zn Auger peak which indicated that some reduction of the ZnO surface occurred with the possible formation of a Pd-Zn bimetallic particle. Similar shifts in the Pd and Zn peaks were observed following reduction under the various conditions.

In contrast to the Pd spectra, shifts in the Fe 2p_{3/2} peak were sensitive to the pretreatment conditions. At reduction temperatures above 250°C, a significant level of zero-valent Fe (Fe⁰) was observed by XPS.

Preliminary Mössbauer studies were conducted with the Pd, Fe/ZnO system to determine if the oxidation state of Fe could be correlated with catalytic

activity. The spectrum obtained for the 1% Pd, 0.3% Fe/ZnO catalyst following reduction at 350°C is given in Figure 1. The best fit obtained for this data indicated the presence of two forms of iron (Fe^0 and Fe^{3+}). At lower reduction temperatures (200°C), Fe^{2+} and Fe^{3+} were the only Mössbauer observable forms of Fe present. Given the low loading levels of Fe and low transmission levels encountered with ZnO in the Mössbauer experiment, the presence of Fe^0 at lower temperatures is not precluded. The absence of observable Fe^0 may be a qualitative indication as to the relative amount of Fe^0 formed at 350°C compared to the amount formed at a lower reduction temperature. In contrast to other Pd-Fe systems, no significant amount of Pd-Fe bimetallic was observed by Mössbauer spectroscopy under any of the reduction conditions employed in this study.

STEM studies on these samples indicate that the average particle size increased from approximately 40 Å to more than 120 Å when pretreatment temperature was raised from 260 to 350°C. Coupled with the observations discussed previously, the decrease in activity observed following reduction above 300°C may be due to a decrease in the amount of Fe^{2+} present in these samples and a sintering of the metallic components.

Pd, Fe Ratio

Whereas a variety of metal loadings levels were employed for this study, the results reported here were all obtained by using a constant 1 wt% Pd loading level. As shown in Table II, increasing the Fe loading resulted in a corresponding increase in catalytic activity. In all cases, the olefin/paraffin ratio was greater than unity. It is also apparent from Table II that the addition of 1 wt% Pd to the supported Fe catalysts did not significantly alter the product distribution, but did result in increased catalytic activity. This behavior is in contrast to Pd, Fe/SiO₂ samples evaluated in our laboratory where Pd addition resulted in a tremendous decrease in olefin to paraffin ratio.

Although Pd/ZnO is a good methanol synthesis catalyst (Table II), it should be noted that very little methanol was observed over the Pd, Fe/ZnO samples. The only apparent effect of Pd addition is to increase the overall catalytic activity of the Fe-based catalyst.

The promotional effect of Pd exhibited in this system may involve increasing the Fe dispersion. High Fe dispersions are difficult to obtain on most supports.(11) In some supported Fe-containing bimetallic systems, the metal particle surface is thought to be enriched in Fe.(12,13) It is conceivable that, in the Pd, Fe/ZnO samples, the bimetallic particles consist of a Pd-rich center covered by an Fe-rich coating. Such a model would explain the apparent lack of methanol production by the Pd component.

Because the product distribution was essentially identical for the Fe/ZnO and Pd, Fe/ZnO catalysts, significant changes in oxidation state of the Fe component were probably not responsible for the increased activity following Pd addition. In fact, the XPS and Mössbauer studies mentioned previously indicate that an increase in the Fe reduction was accompanied by catalyst deactivation.

Chemisorption and microscopy experiments were undertaken in an attempt to further characterize the Pd, Fe/ZnO catalyst. Unfortunately, because of the strong Pd-Zn interaction discussed above, chemisorption results were ambiguous and are not reported here. STEM experiments were also inconclusive, primarily due to difficulties in observing Fe on ZnO.

Temperature and H₂/CO ratio

The apparent activation energies which were measured for the 1% Pd, 0.3% Fe/ZnO

sample between 250-300°C are shown in Table III. For comparison, the activation energies for the 0.3% Fe/ZnO are also given. While the olefin/paraffin ratio decreased slightly with increasing temperature, the olefinic fraction remained above 50 mol% of all products over this temperature range.

The fact that the apparent activation energies for the C₁, C₂, C₃, and C₄ fractions are equivalent implies that formation of a common intermediate, such as CH₂, is the rate-determining step for both CH₄ formation and chain growth to higher molecular weight products.

It is also evident from Table III that the apparent activation energies for the 0.3% Fe/ZnO catalyst were 5-6 Kcal/Mol higher than those measured for the Pd-containing catalyst. If hydrogenation is involved in the rate-determining step, this result indicates that Pd may assist in the activation of H₂ in this catalyst system. This conclusion is supported by the observed H₂ partial pressure dependency (Table IV) for the two separate systems. Addition of Pd to the Fe catalyst resulted in a decrease in reaction order with respect to H₂.

CONCLUSIONS

The addition of Pd to Fe supported on ZnO results in a significant increase in catalytic activity for the conversion of synthesis gas. At the same time, selectivity to olefins remains high over these catalysts. One possible role of Pd addition is to increase the dispersion of the Fe component. Kinetic studies indicate that Pd may also assist in the activation of H₂.

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Table I

XPS Results For 1% Pd, 0.3% Fe/ZnO

<u>Reduction Conditions</u>	<u>Binding Energy, eV*</u>	
	<u>Pd 3d_{5/2}</u>	<u>Fe 2p_{3/2}</u>
Fresh	336.9 ± 0.1	710.7 ± 0.3
H ₂ , 250°C	335.9	710.1
H ₂ , 350°C	336.0	710.3/ 707.0
H ₂ /CO, 260°C	336.0	710.3/ 707.0
CO, 260°C	336.0	710.5

*- Referenced to the Zn 2p_{3/2} peak assigned to be 1021.8 eV

Table II

Effect Of Fe Loading Level On Catalytic Performance
For ZnO Supported Samples

T= 300°C, P= 100 psig, H₂/CO = 1

<u>Metal Loading</u>		<u>Rate (Umoles G⁻¹ S⁻¹) X 10²</u>										
<u>% Pd</u>	<u>% Fe</u>	<u>CH₄</u>	<u>C₂⁼</u>	<u>C₂⁻</u>	<u>C₃⁼</u>	<u>C₃⁻</u>	<u>C₄⁼</u>	<u>C₄⁻</u>	<u>C₅⁼</u>	<u>C₅⁻</u>	<u>CH₃OH</u>	
0.0	0.3	2.5	.65	.42	.78	.10	.37	.11	.23	.15	.31	
1.0	0.3	11.	2.9	1.5	3.3	.43	1.7	.48	.93	.45	.86	
0.0	1.0	13.	3.3	1.8	4.8	.48	2.5	.66	1.7	.87		
1.0	1.0	46.	7.4	12.	15.	3.4	6.6	4.0	3.8	4.8		
0.0	2.5	16.	4.9	2.4	6.9	.67	3.9	.83	2.5	1.1	1.2	
1.0	2.5	48.	9.0	11.	16.	3.0	7.1	3.3	4.3	4.1		
1.0	0.0	---	.01	---	---	---	---	---	---	---	7.18	

C_n⁼ denotes olefin fraction, C_n⁻ denotes paraffin fraction

Table III

Apparent Activation Energies For ZnO Supported Catalysts

$$\text{Rate} = A e^{-E_a/RT}$$

$$(P_{\text{CO}} = P_{\text{H}_2} = 50 \text{ psig, } T = 250\text{--}300^\circ\text{C})$$

Carbon No.	E _a , Kcal/Mol	
	1% Pd, 0.3% Fe	0.3% Fe
1	25	30
2	25	31
3	25	31
4	25	30

Table IV

Reaction Orders For ZnO Supported Catalysts

$$\text{Rate} = k P_{\text{CO}}^N P_{\text{H}_2}^M$$

$$(T = 300^\circ\text{C})$$

Carbon No.	1 % Pd, 0.3 % Fe		0.3% Fe	
	N	M	N	M
1	0.1	0.7	0.8	1.5
2	0.1	0.5	0.9	1.1
3	0.1	0.0	---	---
4	-0.6	-1.5	---	---

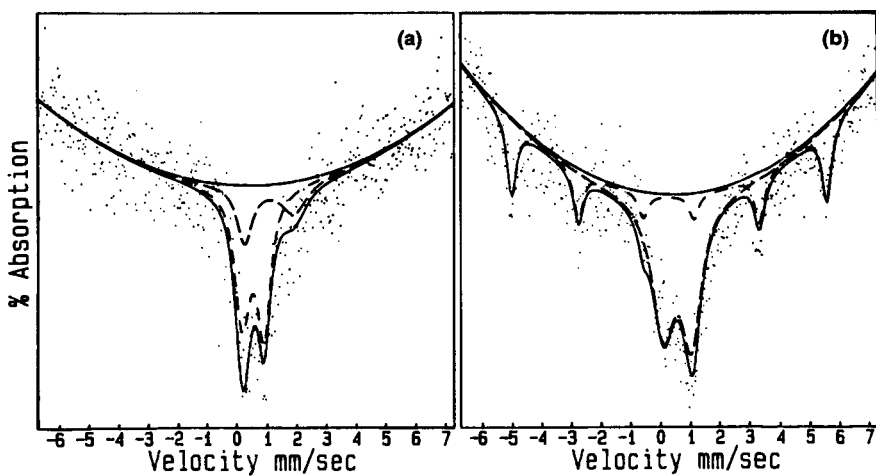


Figure 1. (a) 1% Pd, 0.3% Fe/ZnO Treated in H_2 at $200^\circ C$
(b) 1% Pd, 0.3% Fe/ZnO Treated in H_2 at $350^\circ C$